Thermal Conductivity of Polymer/Nano-filler Blends

S. Ghose[1], K.A. Watson[2], D.M. Delozier[2], D.C. Working[3], J.W.Connell[3], J.G. Smith[3], Y.P.Sun[4] and Y. Lin[4]

[1]NASA Postdoctoral Fellow at NASA Langley

[2] National Institute of Aerospace, Hampton, VA 23666-6147

[3]NASA Langley Research Center, Hampton, VA 23681-2199

[4]Dept of Chemistry, Clemson University, Clemson, SC 26934-0973

Abstract

To improve the thermal conductivity of an ethylene vinyl acetate copolymer, Elvax 260™ was compounded with three carbon based nano-fillers. Multiwalled carbon nanotubes (MWCNT), vapor grown carbon nanofibers (CNF) and expanded graphite (EG) were investigated. In an attempt to improve compatibility between the Elvax and nanofillers, MWCNTs and EGs were modified through non covalent and covalent attachment of alkyl groups. Ribbons were extruded to form samples in which the nano-fillers were aligned, and samples were also fabricated by compression molding in which the nano-fillers were randomly oriented. The thermal properties were evaluated by DSC and TGA, and mechanical properties of the aligned samples were determined by tensile testing. The degree of dispersion and alignment of the nanoparticles were investigated using high-resolution scanning electron microscopy. Thermal conductivity measurements were performed using a Nanoflash™ technique. The thermal conductivity of the samples was measured in both the direction of alignment as well as perpendicular to that direction. The results of this study will be presented.

* To whom correspondence should be addressed: john.w.connell@nasa.gov, (757) 864-4264

THERMAL CONDUCTIVITY OF POLYMER/CARBON NANOFILLER BLENDS

S. Ghose[1], K.A. Watson[2], D.M. Delozier[2], D.C. Working[3], J.W. Connell[3], J.G. Smith, Jr.[3], Y.P. Sun[4] and Y. Lin[4]

[1]NASA Postdoctoral Fellow at NASA LaRC, Hampton, VA 23681-2199
[2] National Institute of Aerospace, Hampton, VA 23666-6147
[3]NASA Langley Research Center, Hampton, VA 23681-2199
[4]Dept of Chemistry, Clemson University, Clemson, SC 26934-0973

Abstract

To improve the thermal conductivity (TC) of an ethylene-vinyl acetate copolymer, Elvax™ 260 was compounded with three types of carbon based nano-fillers: multiwalled carbon nanotubes (MWCNT), vapor grown carbon nanofibers (CNF) and expanded graphite (EG). In an attempt to improve compatibility between Elvax™ and the nanofillers, MWCNTs and EG were modified through non-covalent and covalent attachment of alkyl groups. Ribbons of composites were extruded to form samples in which the nano-fillers were aligned, and samples were also fabricated by compression molding in which the nano-fillers were randomly oriented. Thermal properties of the samples were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and mechanical properties of the aligned samples were determined by tensile testing. Degree of dispersion and alignment of nanoparticles were investigated using high-resolution scanning electron microscopy (HRSEM). TC measurements were performed using a Nanoflash™ technique. TC of the samples was measured in the direction of alignment and perpendicular to alignment. The results of this study will be presented.

Keywords: Elvax™, thermal conductivity, extrusion, functionalization of carbon nanotubes

Corresponding author: Sayata Ghose, fn.s.ghose@larc.nasa.gov, 1-757-864-2094

1. INTRODUCTION

Combining polymers with an organic or inorganic phase to produce a polymer composite is common in the production and processing of modern plastics. The use of nanoscale fillers to prepare polymer nanocomposites (PNC) has been investigated to augment the properties of polymers. PNCs are commonly defined as the combination of a polymer matrix resin and inclusions that have at least one dimension in the nanometer size range [1]. PNCs exhibit significant enhancements in certain properties at a far lower concentration than their conventional micro or macro counterparts. Layered clay, EG, CNF and carbon nanotubes (CNTs) are some of the common nanoparticles used in making PNCs.

CNFs are highly graphitic fibers produced by a catalytic vapor deposition process and have a wide range of morphologies, from disordered bamboo-like formations [2] to highly graphitized "stacked-cup" structures where conical shells are nested within one another [3]. They are widely used as reinforcements for polymers in numerous high-technology applications because of their excellent electrical and thermal properties, high specific tensile strength and modulus [4], improved heat distortion temperatures and increased electromagnetic shielding. Additionally, CNFs are generally more economically attractive than CNTs because of lower manufacturing costs. CNFs have been used as reinforcements for various thermoplastics like polyethylene [5], polypropylene [6,7], polycarbonate [8], nylon [9] and poly(methyl methacrylate) [10].

Graphite is another material commonly used as filler in polymers. It is one of the stiffest materials found in nature with a Young's modulus of ~1060 MPa and also has excellent thermal and electrical properties. This material is currently two orders of magnitude less expensive than CNTs [11]. However graphite exists in large stacks of graphene sheets which requires a prior expansion and exfoliation of the graphene layers to obtain particles with nanometer dimensions. With surface treatment, dispersion of EG in a polymer matrix results in composites with excellent mechanical and electrical properties and high TC. Electrically conductive nanocomposites were prepared by solution intercalation and master batch melt mixing of high density polyethylene (HDPE)/maleic anhydride grafted polyethylene/EG [12]. HDPE was also reinforced with EG and untreated graphite by a melt compounding process that improved electrical and mechanical properties of the EG composite [13]. EG has also been made by oxidation of natural graphite followed by thermal expansion and then mixed with poly(styrene-co-acrylonitrile) to prepare composite sheets [14]. Poly(methylmethacrylate)/EG composites prepared by solution blending methods [15] and aromatic polydisulfide/EG nanocomposites prepared by solution method and hot molding [16] showed good mechanical and electrical properties. The dynamic mechanical and thermal properties of phenylethynyl-terminated polyimide composites reinforced with EG nanoplatelets have also been reported [17].

CNT-based composites are being studied extensively due to the unique physical/mechanical properties of CNTs. CNTs are thought of as the ultimate carbon fibers, and are expected to have high mechanical and electrical properties and ultra high TC [18, 19]. Well dispersed CNTs yield an interconnecting network of nanotubes in a polymer matrix, which provides a conductive pathway for electrical and/or thermal current to flow, resulting in enhanced electrical and thermal properties. However, one of the problems impeding the full realization of CNT properties in composites has been dispersability. Various methods have been attempted for achieving good dispersion of CNTs in a polymer. They include preparation of the polymer in the presence of CNTs under sonication [20], the use of alkoxysilane terminated amide acid oligomers to disperse CNTs [21], melt mixing [22], and shear mixing [23]. Other methods include the use of surfactants and covalent functionalization of various groups. Covalent functionalization has been achieved through either carboxylic acid moieties generated on the CNT surface or by other chemistries providing covalent attachment [24].

Theory predicts the TC (κ) of CNTs at room temperature to be as high as ~6600 W/mK [25] while the experimental value for an individual MWCNT has been reported as 3000 W/mK at room temperature [26]. This value is significantly higher than that of known thermally

conducting materials like diamond (up to 2300 W/mK) and graphite (up to 1960 W/mK). The prominent thermal properties of CNTs have made them promising materials for future applications as thermal management materials, hence it is reasonable to study TC applications of CNTs. Enhancement of TC has been observed in CNT suspensions [27-28] and it is interesting to note that in the case of CNT suspensions, measured TCs are generally greater than theoretical predictions made with conventional heat conduction models. It has been shown in the case of single walled carbon nanotubes (SWCNTs) that TCs exhibit a peak TC that falls off at higher temperatures due to Umklapp scattering [29]. In the case of ordinary carbon-carbon composites, there is a larger mean free path and less phonon-phonon Umklapp scattering causing the TC to increase linearly with heat treatment temperature [30]. However in PNCs, the improvement in TC has always been lower than rule-of-mixture values. In addition to the dispersability issue, another reason that anticipated TC enhancements are not realized is that of thermal interface resistance or Kapitza resistance [31]. This resistance is related to the heat flow barrier between the two phonon spectra and weak contact at the interface, both of which lead to phonon backscattering. One method of reducing this interface problem is by covalent attachment of CNTs to the matrix [32]. Molecular dynamics simulation on SWCNTs showed that functionalization with octane on one out of 15 CNT carbon atoms (~7% functionalization) reduced the thermal interface resistance more than three times. However, it was also reported that these attachments can act as phonon scattering centers themselves and reduce CNT conductivity.

The objective of this work was to achieve an improvement of the TC of the polymer upon addition of nanofiller and to evaluate the effect of alignment on the improved TC values. Elvax™ 260 was chosen as the host resin for trials with various nanoparticles because the resin offers a unique combination of processing and performance characteristics. It provides outstanding toughness and resilience and maintains flexibility over a broad temperature range without the need for plasticizers. The resin can be used alone or blended to improve the flexibility, resilience and toughness of other resins.

Melt compounding was chosen as the method to disperse the nanoparticles in Elvax™ because the technique involves high shear mixing, which helps to disentangle the nanoparticles and disperse them uniformly within the matrix. Melt mixing was followed by extrusion in some of the samples described herein. The process of extruding nanocomposite through a suitable die and subsequent drawing led to continuous ribbons of nanocomposites with substantial orientation of the nanoparticles in the flow direction. Dispersability was assessed by HRSEM and samples were characterized for their thermal and mechanical properties by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), mechanical testing and thermal conductivity analysis. The preparation and characterization of samples containing various loadings of CNTs, CNFs and EGs are discussed.

2. EXPERIMENTAL

2.1 Materials Elvax™ 260, a melt processable ethylene-vinyl acetate copolymer resin obtained from Du Pont, was chosen as the polymer matrix and used as received. MWCNTs, VGE-S12 and

VGE-S16, were procured from the University of Kentucky. CNF, Pyrograph - III - PR-24 HHT was obtained from Applied Sciences, Inc. and EG (Grade 3775) was received from Asbury Carbons. The graphite already had the galleries expanded by first treating with sulfuric acid and then rapidly heating the sample to 900 ºC. The expansion of the graphite was expected to facilitate exfoliation during melt mixing. Anhydrous tetrahydrofuran (THF) was obtained from Fisher. All other chemicals were obtained from commercial sources and used as received.

2.2.1 Non-covalent attachment of 1-dodecylbromide on carbon allotropes (MWCNTs and EG 3775)

To a three-necked round-bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube was charged EG 3775 (20.0 g). The flask was then flame dried under nitrogen and cooled to ambient temperature. 400 mL of tetrahydrofuran (THF) was added and the mixture sonicated at room temperature for 1 h in an Ultrasonik 57X bath operating at ~50% power and degas levels, respectively. 1-dodecylbromide (91.82 g) was then added to the mixture and rinsed in with 50 mL THF and the mixture was stirred under nitrogen at room temperature for 48 h. The product was recovered by vacuum filtration, washed two times with diethyl ether, and air dried at 110 °C overnight to afford 19.7 g of product. By TGA in argon, the loading was 0.1 wt %. A similar process was carried out for MWCNTs.

2.2.2 Covalent attachment of 1-dodecylamine on carbon allotropes (EG 3775)

To a single necked round-bottom flask equipped with a magnetic stir bar and condenser was charged EG 3775 (21.8 g), thionyl chloride (300 g), and N,N-dimethylformamide (2 mL). The mixture was refluxed for 48 h and thionyl chloride removed by distillation. The product was washed with diethyl ether, recovered by vacuum filtration, and dried at 35 °C for 1 h under vacuum. The material (22.31 g) was then added to a three-necked 500 mL round-bottom flask equipped with nitrogen inlet, mechanical stirrer, and drying tube. N,N-dimethylacetamide (200 mL) and 1-dodecylamine (12.8 g) were then added and the mixture was stirred at room temperature under nitrogen for 48 h. The product was recovered by vacuum filtration, washed with ethanol, and air dried at 50 °C overnight in flowing air to afford 22.54 g. By TGA in argon, the loading was 4.1 wt %.

2.3 Processing of Elvax™ 260 with nanofillers

Elvax™ 260 was compounded with MWCNTs, CNFs and EGs in a 60 cc internal mixer (Plasticorder PL2000, Banbury) for 3 h at 25 rpm, 125 °C under N_2 purge. MWCNTs - 20 and 30 wt %, CNFs - 20, 30 and 40 wt %, and EG - 20, 30, and 40 wt % were added to the polymer. During mixing the torque produced was measured and used to calculate the viscosity of the sample. Upon completion of mixing the material was ground in a Mini-Granulator (Kayeness, Inc.) using a 5.5 mm screen. Samples were extruded through a Laboratory Mixing Extruder (LME, Dynisco, Inc.) at a barrel temperature of 50 °C and a die temperature of 125 °C. The dimensions of the die were 0.38 mm x 19.1 mm. The samples were extruded in the form of continuous ribbons that were 0.1-0.5 mm thick, 10-15 mm wide and several meters in length. Once extruded, the ribbons were cut into pieces approximately 2 cm x 2 cm. The pieces were then stacked on one side of a 9 cm x 2 cm x 3 cm (i.d.) mold and the remainder of the mold was filled with Elvax™ 260 pellets. The stacked ribbons were compression molded at 80 °C and 1.72 MPa for 3 h. The molded samples were then sliced using an Isomet low speed saw with a diamond wafering blade 12.7 cm diameter and 0.5 mm thick with 30 HC diamond (Buehler Ltd). Unoriented samples were made using a Laboratory Mixing

Molder (LMM Dynisco, Inc.) and a rectangular mold (1.52 mm x 38.1 mm x 1.27 mm). A rough blend of materials was added to the mixing bowl of the LMM kept at 125 ^{o}C and maintained for 0.5 h. The blend was then dynamically pressed at a rotational speed of 100% of ram-motor capacity and then static pressed to degas, before passing through the nozzle orifice (~1.6 mm) into the rectangular mold kept at 125 ^{o}C. The material was then manually compressed at a pressure of ~ 4.5 kN and set under pressure from the ram while being air cooled. Tubes were extruded through a Laboratory Mixing Extruder (LME, Dynisco, Inc.) at a barrel temperature of 50 °C and a die temperature of 130 °C. The dimensions of the die were an o.d. of 0.3175 cm (1/8") and an i.d. of 0.1588 cm (1/16").

2.5 Characterization HRSEM images were obtained using a Hitachi S-5200 field emission scanning electron microscope (FE-SEM) equipped with a "through-the-lens" secondary electron detector. Thin-film tensile properties were determined according to a modified version of ASTM D882 using either four or five specimens (0.51 cm wide) per test conditions using an Eaton Model 3397-139 11.4 kg load cell on a Sintech 2 test frame. The test specimen gauge length was 5.1 cm and the crosshead speed for film testing was 0.51 cm/minute. Thermal diffusivity of the molded samples as well as ribbons was measured at 25 ^{o}C using a Netzsch LFA 447 NanoFlash according to ASTM E1461, "Standard Test Method for Thermal Diffusivity by the Flash Method". Sample sizes of 1 cm x 1 cm were cut by precision sectioning saw (Buehler Isomet 1000, series 30 HC diamond wafering blade). Sample density was calculated by measuring sample dimensions and weight. Specific heat of the test sample was measured by comparing the temperature rise of the sample to the temperature rise of a standard reference sample (Pyrex, TC ~ 1.09 W/mK, Cp ~ 0.76 J/gk) tested under the same conditions. The steady-state TC was calculated through the equation

$$\lambda = C_p D \rho$$

where λ is TC, D is thermal diffusivity, C_p is specific heat and ρ is the material density. Samples were sprayed with a thin layer of graphite (for uniform thermal adsorption), which was easily rinsed away by solvent (e.g., methanol).

3. RESULTS AND DISCUSSION

3.1 Modification of MWCNTs and EG 3775 MWCNTs and EG 3775 were modified with aliphatic groups through non-covalent (electrostatic) and covalent attachment. Electrostatic attachment was accomplished with 1-dodecylbromide and generally resulted in less than 0.5 wt % loading. An approximate order of magnitude increase in loading was observed with the covalent attachment of 1-dodecylamine through an amide linkage resulting from the reaction of the acid chloride modified carbon allotrope and the aliphatic amine. TGA data for all wt% loadings of the aliphatic group were obtained from data taken at 500 °C; a temperature at which the organic (aliphatic) groups would be burnt off without affecting the nanofillers. The various modifications to EG 3775 are shown in Figure 1.

3.2 Processing of Elvax™ 260/nanofillers Torque values were obtained during mixing in the Plasticorder and were used to calculate the melt viscosities of the samples. Table 1 denotes the calculated melt viscosities of the various samples at a shear rate of 92.5 sec^{-1} and a temperature of 125 °C. The neat resin had the lowest viscosity and these values increased with increasing

nanofiller loading. However, modification of the nanofiller lowered the viscosity. Figure 2 shows a picture of a typical extruded ribbon. The primary purpose of extrusion was to align the nanofillers in the flow direction. Stacked ribbons were molded and samples obtained by cutting the molded block in the direction of the dotted line in Figure 3 using a diamond saw. In this way samples were obtained with alignment both parallel and perpendicular to the direction of conductivity measurement. Figure 4 shows the extruded tubes containing Elvax™ 260/nanofillers. Some alignment of the nanofillers in these tubes was expected although it might not be to the extent as with the extruded ribbons.

3.3 HRSEM of extruded ribbons Figure 5(a) shows the image of the 30 wt% MWCNT melt mixed ribbon while Figure 5(b) shows the 10 wt% MWCNT ribbon. In both cases, it was observed that the MWCNTs were aligned in the direction of flow (indicated by the arrow). Figures 5(c) and (d) show the alignment at two CNF loading levels. Here too, there is significant alignment of the nanofibers in the extrusion direction. HRSEM images were obtained for the 30 and 40 wt% EG extruded ribbon (Figure 5 (e & f)). The graphite platelets were visible at high voltages. The platelets vary in size but are all under 1 μm in one dimension. The particles appeared to be well dispersed throughout the polymer. Figure 6(a) shows the HRSEM images of the outer surfaces of the Elvax™ 260/MWCNT extruded tubing. The nanotubes are significantly aligned in the direction of extrusion denoted by the arrow. Figure 6(b) is the cross section of the tubing and MWCNTs can be seen projecting out of the polymer matrix.

3.4. Mechanical properties of extruded ribbons Mechanical properties were measured on Elvax™ 260/nanofiller composites with the results shown in Table 2. The strips used for testing were cut from ribbons prepared from extrusion; hence the nanofillers are somewhat in alignment in the stress direction. The results should be viewed with care because the measurement of the ribbon thickness was not accurate due to uneven ribbon surfaces. As expected, with increased filler loading level, modulus increased and elongation decreased. For a loading level of 20 and 30 wt%, CNF and EG samples showed an increase in strength with increased loading level while the reverse was observed for the MWCNT samples. The modified MWCNT and EG samples exhibited lower mechanical properties compared to the unmodified sample.

3.5 Thermal conductivity measurements Since the structure of nanotubes is anisotropic in space, the electrical and thermal properties should be different in the axial (parallel to nanotube axis) and transverse (perpendicular to nanotube axis) directions. There have been a few reports on the use of dispersed CNTs as thermally conducting fillers in polymer composites and certain enhancements in TC were observed [25, 33]. However, the enhanced values are typically below those predicted by the rule of mixtures. One probable reason for this is the existence of interface thermal resistance between the overlaps in the CNT passage leading to a rapid increase in overall thermal resistance [34]. Huang et al. [33] proposed a composite structure where all the CNTs embedded in the matrix are aligned from one surface to the opposite side with all the CNT surfaces revealed on both surfaces. This structure leads to high TC since the CNTs form ideal thermally conducting pathways. Low thermal interface resistances can also be expected as the protruding tips would ensure better thermal contact. It has been reported that alignment of nanofillers in the polymer matrix leads to enhancement of TC [30, 35]. Based on the literature

survey to date, it was decided to process samples with significant nanofiller alignment and measure TC both in the direction and perpendicular to the direction of alignment (nanotube axis).

Four types of Elvax™ 260/nanofiller samples were measured for TC. These were the extruded ribbon, molded samples cut perpendicular to flow direction, samples with no alignment and extruded tubes. For the extruded ribbons the TC was measured perpendicular to the direction of nanotube alignment. Table 3a denotes the values for neat Elvax™ 260 and Elvax™ 260/nanofiller samples. The TC increased with increasing loading level of nanofillers. The highest TC was observed in the 20 wt% modified MWCNT samples and the conductivity increased by 180 % with respect to the neat material. The modified MWCNT sample had a higher TC value compared to the unmodified sample having the same loading level. However, the same trend was not observed in the case of modified EG samples.

The second set of samples was the molded samples where the TC was measured in the direction of nanofiller alignment. Table 3b shows the values for the neat molded sample as well as Elvax™ 260/nanofiller samples. This data has also been shown in a plot (Figure 7a). The TC of the samples was observed to be significantly greater in the direction of alignment (Table 3b) compared to those that were perpendicular to the direction of alignment (Table 3a). The MWCNT samples at 30 wt% loading exhibited a 9.1-fold increase in TC relative to neat Elvax™ whereas the CNF samples loaded at 40 wt% showed a 12.1-fold increase. The largest TC increase, 17.1-fold, was exhibited by 40 wt% loading of EG samples. The data indicates that the nanofillers, when aligned, form a network that successfully conducts heat by perhaps enabling a more efficient phonon transfer from one filler particle to another. Comparing neat and modified MWCNTs, it was observed that TC shows a 10.5-fold improvement upon modification compared to a 7-fold improvement in the unmodified sample. However, for the modified EG sample, the improvement in TC was 14-fold compared to 17-fold for the unmodified material.

The highest TC value for unoriented samples (Table 3c) was exhibited by 50 wt% modified EG sample that showed a 7.6-fold increase in TC. Again, modified MWCNT samples showed higher TC values compared to the unmodified ones while the opposite was observed for modified EG samples. The TC results from the LMM samples proved conclusively that alignment of nanofillers in the polymer matrix significantly raises the TC of the samples. However, unaligned samples also show a significant improvement and may be useful in applications when it is not possible to achieve nanoparticle alignment in a desired direction.

The TC was measured for extruded tubes as well (Figure 7b). HRSEM revealed alignment of the nanofillers along the length of the tubes and the TC measurements were also made in the direction of the tube axis. As seen in Table 3d, 30 wt% loading of MWCNT improves the TC 17-fold while the same loading of CNF improved TC 13.5-fold. For 40 wt% EG samples, the improvement was 21-fold. Both modified MWCNTs and EGs improved the TC compared to unmodified nanofillers. In contrast to ribbons and LMM samples, the extruded composite tubes had elevated TC after modification of the EG. Apart from the improved TC, the other characteristic that needed to be studied for these tubes was their flexibility.

3.6 Radius of curvature of tubing Flexibility of the extruded tubes was tested by using a series of stainless steel cylinders of varying diameter. Each tube was wound around the cylinder of a particular diameter and the smallest diameter that the tube could be wound around without kinking was noted. Table 4 shows the data from the flexibility tests. It was observed that at loading levels of 20 and 30 wt%, CNF filled Elvax™ 260 had the highest flexibility and the EG filled polymer had the least. At a loading level of 40 wt%, the samples show poor flexibility. However, modification of the nanofillers yielded a significant improvement on the flexibility as seen in the cases of the 20 wt% modified MWCNT and the 40 wt% modified EG. In both cases modification improved the flexibility and TC. It was possible that the alkyl groups provided a plasticizing effect. From the data it was evident that unmodified samples with high filler loadings and hence high TC values had lower flexibilities. Typically the EG filled samples had higher TC but as evident from Figure 8, they also showed kinking. Hence the loading level of nanofiller must be optimized in order to achieve a balance between the TC and the flexibility.

4. SUMMARY

Elvax™ 260 was mixed with three different carbon-based nanofillers in efforts to increase the TC of the polymer. After initial mixing, the nanocomposites were extruded or processed via the LMM process. HRSEM revealed significant alignment of the nanofillers in the extruded samples. TC measurements were made both in the direction and perpendicular to the direction of alignment of nanofillers, for tubes along the length as well as for unaligned samples. For ribbon samples, it was found that the largest improvement in TC was achieved in the case of aligned samples when the measurement was performed in the direction of alignment. Unaligned samples also showed an improvement in TC and may be useful in applications when it is not possible to align the nanofiller. For extruded ribbons and molded samples, modification of MWCNTs led to significant improvement in the TC value compared to the composite containing unmodified MWCNTs but this behavior was not seen for the modified EG sample. However, for tubes containing modified nanofillers, improvement in both TC and flexibility were observed. When all four types of samples were compared, the extruded tubes showed the highest TC. Improvements in TC did not approach those expected based on a rule of mixtures and this is likely due to poor phonon transfer through the matrix. Finally when the TC, flexibility and cost of material were taken into consideration, it may be concluded that for 20 and 30 wt% loading levels of unmodified nanofillers, the CNF samples provide the best properties – the samples had excellent flexibility, reasonably high TC and cost substantially less than MWCNTs.

5. ACKNOWLEDGEMENT
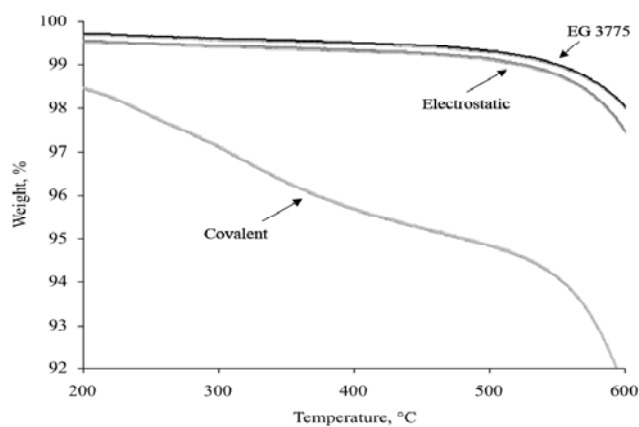
6. FIGURES AND TABLES

Figure 1: TGA in argon of EG 3775 (pristine), electrostatic (1-dodecylbromide), and covalent (1-dodecylamine) modification.

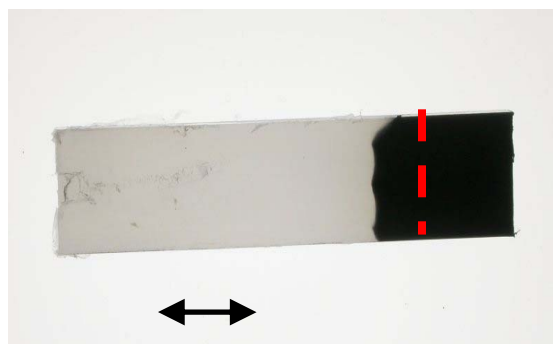Figure 2: Ribbon of Elvax™ 260/MWCNTs

Figure 3: Plaque showing cut direction and nanofiller alignment (arrow)

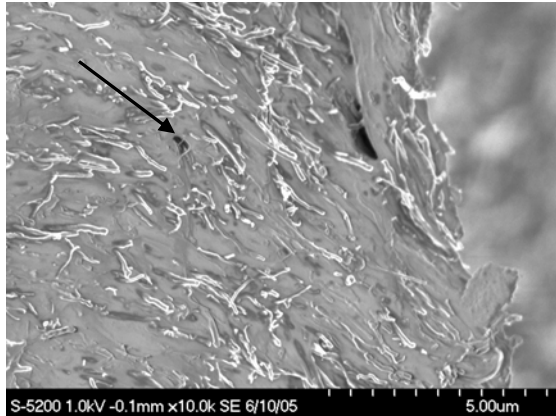Figure 4: Extruded tubes of Elvax™ 260/MWCNTs

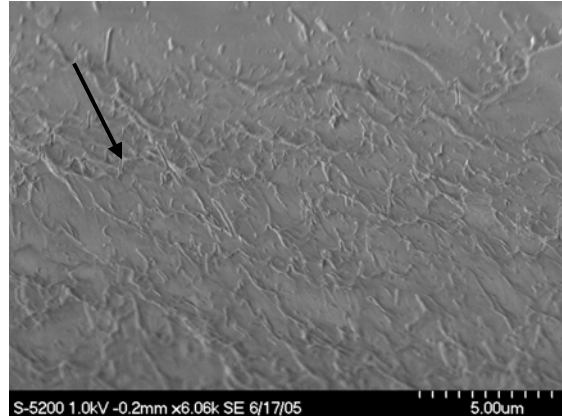Figure 5(a): 30 wt% MWCNT
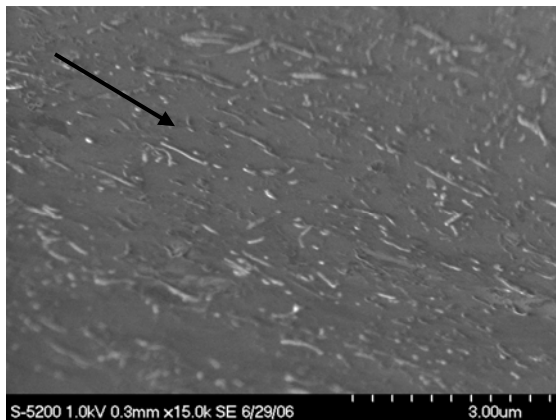

Figure 5(b): 10 wt% MWCNT
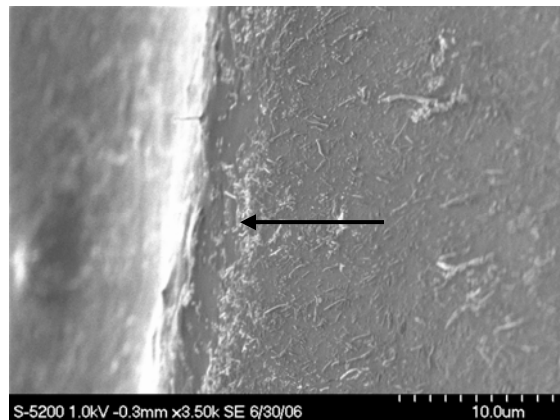

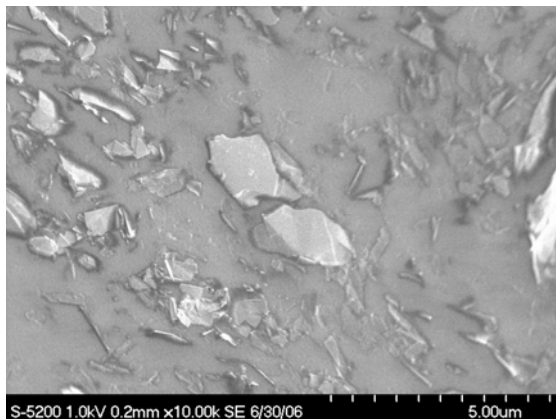Figure 5(c): 30 wt% CNFs

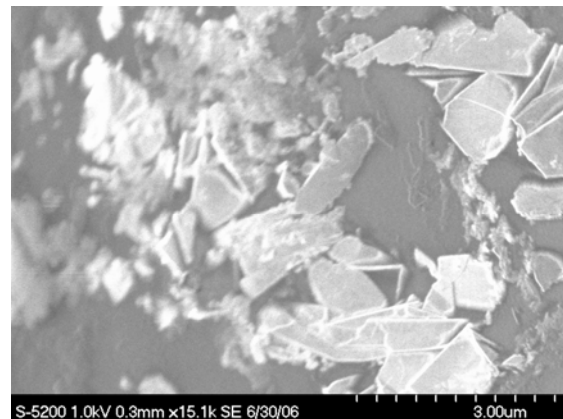Figure 5(d): 40 wt% CNF

Figure 5(e): 30 wt% EG

Figure 5(f): 40 wt% EG

Figure 5: HRSEM of Elvax™ 260/nanofiller ribbon sample; arrow denotes direction of flow

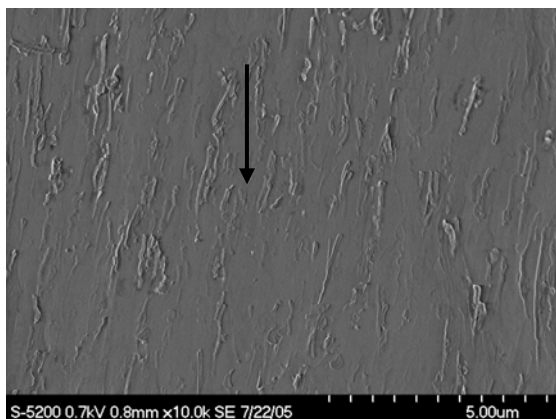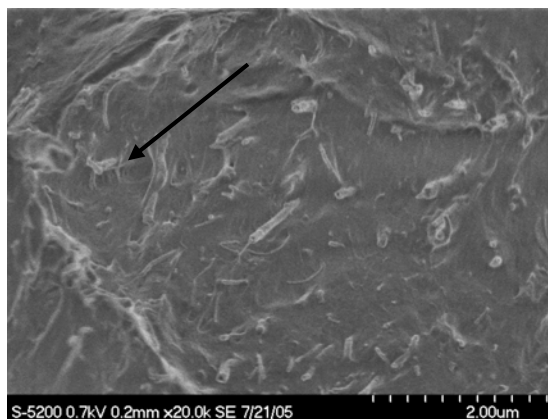Figure 6(a): 30 wt% MWCNT

Figure 6(b): 20 wt% MWCNT

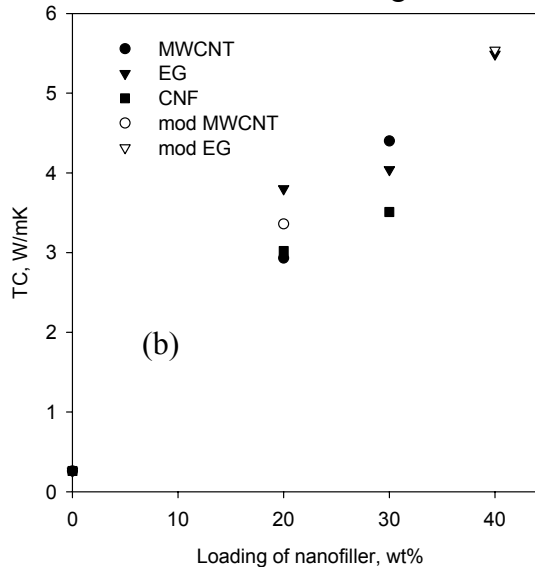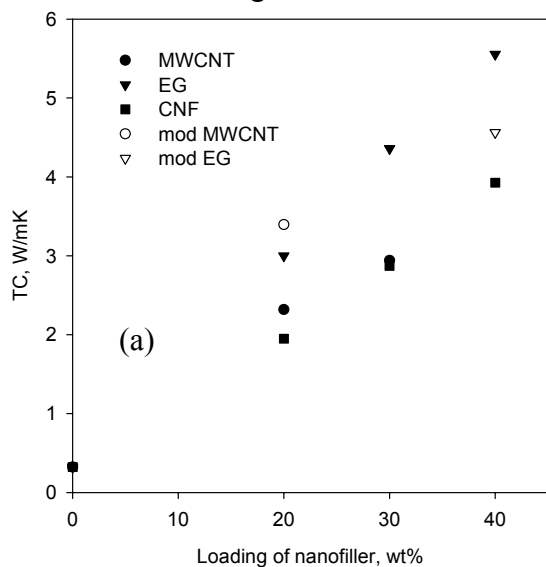Figure 6: HRSEM of surfaces of Elvax™ 260/MWCNT tubing

Figure 7: Thermal conductivity of molded Elvax™ 260/nanofiller samples; measurement along direction of alignment in molded samples (a) and in tubes (b)

Figure 8(a): No kinks – 30 wt % MWCNT

Figure 8(b): Kinking – 30 wt % EG

Figure 8: Radius of curvature of Elvax™ 260/nanofiller tubing

Table 1: Melt viscosities of Elvax™ 260/nanofiller samples:

Sample	Viscosity (poise)
Neat Elvax™ 260	10010
Elvax ™, 20 wt% MWCNT	18779
Elvax ™, 20 wt% mod MWCNT	15615
Elvax ™, 30 wt% MWCNT	22689
Elvax ™, 20 wt% CNF	14616
Elvax ™, 30 wt% CNF	18002
Elvax ™, 40 wt% CNF	22993
Elvax ™, 20 wt% EG	10984
Elvax ™, 30 wt% EG	12755
Elvax ™, 40 wt% EG	13465
Elvax ™, 40 wt% mod EG*	------

Shear rate: 92.5/sec, Temperature: 125 ^{o}C
* Torque value went off scale

Table 2: Mechanical properties of Elvax™ 260/nanofiller samples:

Sample	Modulus, GPa	Strength, MPa	Elong., %
Neat Elvax™ 260	0.01 ±0.001	9.7 ± 0.1	856 ± 102
Elvax ™, 20 wt% MWCNT	0.07 ± 0.01	11.1 ± 2.0	586 ± 45
Elvax ™, 20 wt% mod MWCNT	0.06 ± 0.01	9.0 ± 1.6	481 ± 209
Elvax ™, 30 wt% MWCNT	0.12 ± 0.01	10.2 ± 4.0	274 ± 93
Elvax ™, 20 wt% CNF	0.05 ± 0.01	11.3 ± 0.3	710 ± 54
Elvax ™, 30 wt% CNF	0.09 ± 0.01	11.9 ± 0.4	537 ± 4
Elvax ™, 40 wt% CNF	0.13 ± 0.01	8.1 ± 0.3	97 ± 20
Elvax ™, 20 wt% EG	0.06 ± 0.01	7.7 ± 1.1	430 ± 65
Elvax ™, 30 wt% EG	0.10 ± 0.01	8.9 ± 0.7	164 ± 44
Elvax ™, 40 wt% EG	0.18 ± 0.02	11.9 ± 2	77 ± 8
Elvax ™, 40 wt% mod EG	0.12 ± 0.01	8.5 ± 2.4	97 ± 16

Table 3a: TC of Elvax™ 260/nanofiller extruded ribbons*:

Sample	Thermal Conductivity, W/mK
Neat Elvax™ 260	0.311
Elvax ™, 20 wt% MWCNT	0.356
Elvax ™, 20 wt% mod MWCNT	0.573
Elvax ™, 30 wt% MWCNT	0.469
Elvax ™, 20 wt% CNF	0.409
Elvax ™, 30 wt% CNF	0.486
Elvax ™, 40 wt% CNF	0.611
Elvax ™, 20 wt% EG	0.399

Elvax ™, 30 wt% EG	0.509
Elvax ™, 40 wt% EG	0.544
Elvax ™, 40 wt% mod EG	0.444

*TC measurement is perpendicular to alignment

Table 3b: TC of Elvax™ 260/nanofiller molded samples*:

Sample	Thermal Conductivity, W/mK
Neat Elvax™ 260	0.324
Elvax ™, 20 wt% MWCNT	2.318
Elvax ™, 20 wt% mod MWCNT	3.395
Elvax ™, 30 wt% MWCNT	2.942
Elvax ™, 20 wt% CNF	1.949
Elvax ™, 30 wt% CNF	2.872
Elvax ™, 40 wt% CNF	3.926
Elvax ™, 20 wt% EG	3.000
Elvax ™, 30 wt% EG	4.359
Elvax ™, 40 wt% EG	5.554
Elvax ™, 40 wt% mod EG	4.562

* TC measurement is parallel to alignment

Table 3c: TC of Elvax™ 260/nanofiller LMM samples (unoriented):

Sample	Thermal Conductivity, W/mK
Neat Elvax™ 260	0.324
Elvax ™, 20 wt% MWCNT	0.555
Elvax ™, 20 wt% mod MWCNT	0.655
Elvax ™, 30 wt% MWCNT	0.705
Elvax ™, 20 wt% CNF	0.634
Elvax ™, 30 wt% CNF	0.643
Elvax ™, 20 wt% EG	0.666
Elvax ™, 30 wt% EG	0.902
Elvax ™, 40 wt% EG	1.369
Elvax ™, 40 wt% mod EG (covalent)	1.030
Elvax™, 50 wt% mod EG (non-covalent)	2.460

Table 3d: TC of Elvax™ 260/nanofiller tube samples:

Sample	Thermal Conductivity, W/mK
Neat Elvax™ 260	0.26
Elvax ™, 20 wt% MWCNT	2.93
Elvax ™, 20 wt% mod MWCNT	3.36
Elvax ™, 30 wt% MWCNT	4.40
Elvax ™, 20 wt% CNF	3.02
Elvax ™, 30 wt% CNF	3.51
Elvax ™, 20 wt% EG	3.80
Elvax ™, 30 wt% EG	4.04
Elvax ™, 40 wt% EG	5.49
Elvax ™, 40 wt% mod EG	5.54

Table 4: Radius of Curvature of Elvax™ 260/nanofiller tubing:

Diameter, Inches	20 wt % MWCNT	30 wt % MWCNT	20 wt% CNF	30 wt% CNF	40 wt% CNF	20 wt% EG	30 wt% EG	40 wt% EG	40 wt% mod EG	20 wt% mod MWCNT
1.644	√	√	√	√	x	√	√	x	√	√
1.486	√	√	√	√	x	√	√	x	√	√
1.410	√	√	√	√	x	√	√	x	√	√
1.289	√	√	√	√	x	√	√	x	√	√
1.263	√	√	√	√	x	√	x	x	√	√
1.174	√	x	√	√	x	x	x	x	x	√
1.124	√	x	√	√	x	x	x	x	x	√
1.009	x	x	√	√	x	x	x	x	x	√
0.954	x	x	√	√	x	x	x	x	x	√

√ - no kinking ; x - kinking

7. REFERENCES

1. Collister J, Polymer Nanocomposites: Synthesis, Characterization and Modeling, 2002, Ed. R. Krishnamoorti and R.A. Vaia, ACS Symposium Series 804.
2. Merkulov VI, Lowndes DH, Wei YY, Eres G and Voelkl E, 2000, *Appl. Phys. Lett.*, **76**(24), 3555.
3. Endo M, Kim YA, Hayashi T, Fukai Y, Oshida K, Terrones M, Yanagisawa T, Higaki S and Dresselhaus MS, 2002, *Appl Phys Lett,* **80**(7), 1267.
4. Hammel E, Tang X, Trampert M, Schmitt T, Mauthner K, Eder A and Potschke P, 2004, *Carbon*, **42**, 1153.
5. Lozano K, Yang S and Zeng Q, 2004, *J. Appl. Poly. Sci.*, **93**, 155.

6. Kuriger RJ, Alam MK, Anderson DP and Jacobsen RL, 2002, *Composites, Part A*, **33**, 53-62.

7. Lozano K, Bonilla-Rios J and Barrera EV, 2001, *J. Appl. Poly. Sci.*, **79**, 125.

8. Carneiro OS, Covas JA, Bernardo CA, Caldeira G, Van Hattum FWJ, Ting JM, Alig RL and Lake ML; 1998, *Composites Sci. Tech.*, **58**, 401.

9. Pogue RT, Ye J, Klosterman DA, Glass AS and Chartoff RP, 1998, *Composites: Part A*, **29**, 1273.

10. Cooper CA, Ravich D, Lips D, Mayer J and Wagner HD, 2002, *Composites Sci. Tech.*, **62**, 1105.

11. Drzal LT and Fukushima H, Unites States Patent Application Publication, Pub No. US20040127621 (2004).

12. Shen JW, Huang WY, Zuo SW and Hou J, 2005, *J. Appl. Polym. Sci.*, **97**, 51.

13. Zheng W, Lu X and Wong SC, 2004, *J. Appl. Polym. Sci.*, **91**, 2781.

14. Zheng G, Wu J, Wang W and Pan C, 2004, *Carbon*, **42**, 2839.

15. Zheng W, Wong SC and Sue HJ, 2002, *Polymer*, **73**, 6767.

16. Song LN, Xiao M, Li XH and Meng YZ, 2005, *Mater. Chem. Phys.*, **93**, 122.

17. Cho D, Lee S, Yang G, Fukushima H and Drzal LT, 2005, *Macromol. Mater. Eng.* **290**, 179.

18. Gao X, Liu L, Guo Q, Shi J and Zhai G, 2005, *Materials Letters*, **59**, 3062.

19. Lau KT and Hui D, 2002, *Composites Part B: Engineering*, **33**, 263.

20. Park C, Ounaies Z, Watson KA, Crooks RE, Smith Jr. JG, Lowther SE, Connell JW, Siochi EJ, Harrison JS and St. Clair TL, 2002, *Chem. Phys. Lett.* **364**, 303.

21. Smith Jr. JG, Connell JW and Hergenrother PM, 2001, *Soc. Adv. Matl. and Proc. Eng. Proc.*; **46**: 510.

22. Haggenmueller R, Gommans HH, Rinzler AG, Fischer JE and Winey KI, 2000, *Chem Phys Lett;* **330**, 219.

23. Andrews R, Jacques D, Minot M and Rantell T, 2002, *Macromol. Mater. Eng.*, **287**(6), 395.

24. Banerjee S, Hemraj-Benny T and Wong SS, 2005, *Adv. Mater.*, **17**(1), 17.

25. Liu CH, Huang H, Wu Y and Fan SS, 2004, *Appl. Phys. Lett.*, **84**, 4248.

26. Kim P, Shi L, Majumdar A and McEuen PL, 2001, *Phys. Rev. Lett.,* **87** (21), 215502.

27. Hwang YJ, Ahn YC, Shin HS, Lee CG, Kim GT, Park HS and Lee JK, 2005, *Current Appl. Phys.* article in press (available online August 19, 2005).

28. Choi SUS, Zhang ZG, Yu W, Lockwood FE and Grulke EA, 2001, *Appl. Phys. Lett.,* **79**, 2252.

29. Osman MA and Srivastava D, 2001, *Nanotechnology*, **12**, 21.

30. Gong Q, Li Z, Bai X, Li D, Zhao Y and Liang J, 2004, *Mater. Sci. Eng.A,* **384**, 209.

31. Shenogin S, Xue L, Ozisik R and Keblinski P, 2004, *J. Appl. Phys.*, **95**(12), 8136.

32. Shenogin S, Bodapati A, Xue L, Ozisik R and Keblinski P, 2004, *Appl. Phys. Lett.*, **85**(12), 2229.

33. Huang H, Liu C, Wu Y and Fan S, 2005, *Adv. Mater. (Communications)*, **17**, 1652.

34. Huxtable ST, Cahill DG, Shenogin S, Xue L, Ozisik R, Barone P, Usrey M, Strano MS, Siddons G, Shim M and Keblinski P, 2003, *Nat. Mater.*, **11**, 731.

35. Chen YM and Ting JM, 2002, *Carbon*, **40**, 359.